Anomalous magnetic ordering in $PrBa_2Cu_3O_{7-y}$ single crystals: Evidence for magnetic coupling between the Cu and Pr sublattices

V.N. Narozhnyi [a,b,1], D. Eckert [b], K.A. Nenkov [b,2], G. Fuchs [b], T.G. Uvarova [c], K.-H. Müller [b]

[a] *Institute for High Pressure Physics, Russian Academy of Sciences, Troitsk, Moscow Region, 142092, Russia*

[b] *Institut für Festkörper- und Werkstofforschung Dresden e.V., Postfach 270016, D-01171 Dresden, Germany*

[c] *Institute of Crystallography, Russian Academy of Sciences, Leninski pr. 59, Moscow, 117333, Russia*

Abstract

In Al-free $PrBa_2Cu_3O_{7-y}$ single crystals the kink in the temperature dependence of magnetic susceptibility $\chi_{ab}(T)$, connected with Pr antiferromagnetic ordering, disappears after field cooling (FC) in a field $H \parallel ab$-plane. The kink in $\chi_c(T)$ remains unchanged after FC in $H \parallel c-$axis. As a possible explanation, freezing of the Cu magnetic moments, lying in the $ab-$plane, caused by FC in $H \parallel ab$, hinders their reorientation and, due to coupling between the Pr and Cu(2) sublattices, ordering of the Pr^{3+} moments. A field induced phase transition and a field dependence of the Pr^{3+} ordering temperature have been found for both $H \parallel c$ and $H \parallel ab$.

PACS numbers: 74.72.Bk, 75.50.Ee, 75.25.+z, 75.30.Gw

Key words: Antiferromagnetic order; Magnetic susceptibility; Magnetization; Single crystal; $PrBa_2Cu_3O_{7-y}$,

[1] Corresponding author: Tel.: +7 095 334 08 08; Fax: +7 095 334 00 12; E-mail: narozh@ns.hppi.troitsk.ru

[2] On leave from International Laboratory of High Magnetic Fields and Low Temperatures, Wroclaw, Poland

1 Introduction

$PrBa_2Cu_3O_{7-y}$ (Pr-123) is the anomalous member among the orthorhombic fully doped $R Ba_2Cu_3O_{7-y}$ (R =Y, rare earth) cuprates (see Ref. [1–3] for a review). The transition temperature T_N for antiferromagnetic (AFM) ordering of the Pr magnetic moments, usually accepted as 17 K, [4,5] is one or two orders of magnitude higher than exhibited by the other members of that series. Moreover, magnetic ordering in the Cu(2) sublattice was found at $T \approx 280$ K even though the compound is oxygen rich [6]. It was generally believed that Pr-123 is the only nonsuperconducting compound in that row, but very recently an indication on superconductivity was reported for Pr-123 grown by the traveling-solvent floating-zone method [7], see also Ref. [8]. This result is in sharp contrast to those obtained for crystals grown by the flux method (see Comment [9] on Ref. [7]) and more work is necessary to clarify the situation.

Several models have been proposed to explain the absence of superconductivity in Pr-123 including (i) a valence of the Pr ion considerably greater than +3, (ii) magnetic pair breaking, (iii) Pr ions on Ba sites [8], and (iv) hybridization of Pr and CuO_2 layers (see, e.g., [1–3]). The situation with the Pr valence in Pr-123 is not completely clear up to now, see, e.g., Ref. [10], although strong evidence was obtained from inelastic neutron scattering [2] and spectroscopic data [3] for the predominance of +3 valence of Pr and Pr $4f$–O $2p_\pi$ hybridization. This hybridization should not only lead to the suppression of superconductivity but also to a considerable enhancement of the exchange interaction between the Pr^{3+} magnetic moments resulting in (i) a stabilization of the low-temperature non-zero value of these moments (which would vanish for dominating crystal field interactions) and (ii) an increase of T_N.

Although a λ-type anomaly at T_N was found from specific heat measurements [4,5,11], the magnetic susceptibility χ of Pr-123 continues to increase with decreasing temperature T even below T_N, [4,5,2,12,13] contrary to the decrease of χ below T_N usually observed for AFM ordering. Only a weak change of the slope in the $\chi(T)$ dependence was found even for single crystals. In the first neutron diffraction study [4] a simple magnetic structure was proposed in which the Pr moments (0.74 μ_B) point along the orthorhombic c axis and alternate antiferromagnetically in all three crystallographic directions. On the other hand, Mössbauer spectroscopy [14] revealed AFM ordering with the moments tilted away from the c axis by an angle θ=65°. Tilting of magnetic moments has been also found by neutron diffraction [15]. All these results were questioned by the authors of NMR experiments [16], concluding that the Pr moment lies in the ab-plane and is only 0.017 μ_B. This work was recently strongly criticized by Boothroyd *et al.*, [17] who have investigated Al-free single crystals by neutron diffraction and found θ=35° and μ_{Pr}=0.56 μ_B. Moreover they observed, that the Pr ordering is accompanied by a counterrotation

of the antiferromagnetic arrangement on the bilayer CuO_2 planes about the c axis with establishing of a noncollinear ordering of Cu moments below T_N. It was underlined [17] that from symmetry considerations the coexistence of magnetic order on the *coupled* Pr and Cu sublattices is not only consistent with, but even *requires* a reorientation of the Cu magnetic structure during Pr magnetic ordering, see also Ref. [18].

These reported results show, that the nature of magnetic ordering in Pr-123 is rather complicated. Previous magnetic measurements [12,13] were performed on crystals grown in alumina crucibles, which leads to dissolving of Al in the sample. It is well known, that Al impurities can considerably influence the properties of cuprates (see, e.g., [15]). In the present work we have studied the magnetic properties of high quality Al-free Pr-123 single crystals.

2 Experimental

Pr-123 single crystals were grown in Pt crucibles by the flux method [19]. Electron-probe microanalysis has shown that the concentration of impurities in the crystals does not exceed the detection limit of the instrument used (~ 1 at. %). Lower traces of impurities and especially of Pt can not be excluded. (The only known crucible's material that can give the ppm level of detrimental impurities in the flux grown Pr-123 crystals is unreactive $BaZrO_3$ [20]). X-ray analysis has revealed single phase twinned orthorhombic material with lattice parameters a=3.868, b=3.911, and c=11.702 Å. The crystals were annealed at T=450° in oxygen flow during one week. Two samples with the dimensions $\approx 1.2 \times 1 \times 0.2$ mm^3 and masses of 1.48 and 1.40 mg have been investigated. Very similar results have been obtained for both crystals. The magnetization of the samples with field parallel (M_c) and perpendicular (M_{ab}) to the c-axis was measured at 1.7 K $\leq T \leq$ 300 K and $H \leq$ 48 kOe by a Quantum Design SQUID magnetometer. Magnetic susceptibility (determined as, e.g., $\chi_c(T) = M_c(T)/H$) has been measured typically at H=10 kOe.

3 Results and discussion

The temperature dependence of the inverse magnetic susceptibility is shown in Fig. 1 for the both directions of H. The best fits of the data for 50 K $\leq T \leq$ 300 K to a modified Curie-Weiss law including a temperature independent χ_0, see Ref. [2], are shown by lines in Fig. 1. The values of the Pr effective paramagnetic moment obtained from this fit are 2.9 and 3.1 μ_B for $H||ab$ and $H||c$, respectively. These values are in good agreement with previously published data for poly- and single crystals [4,5,2,12,13] as well as with

calculations of $\chi(T)$ based on the results of inelastic neutron scattering [2] and taking into account the effect of crystalline electric field (CEF) splitting of the Pr^{3+} free ion multiplet. The obtained values of $\chi(300$ K$)$ are also in agreement with these calculations for Pr^{3+} and are approximately two times greater than the calculated value [2] for Pr^{4+}. The observed sign of magnetic anisotropy ($\chi_c > \chi_{ab}$) corresponds to the schemes of CEF splitting of the low lying quasitriplet (well separated from higher levels of Pr^{3+}) proposed in Refs. [2] and [21]. The other sign of anisotropy ($\chi_c < \chi_{ab}$) was proposed by assuming another scheme of levels [22]. This result is not in agreement with our data. It should be noted, that the conclusions from NMR experiments, [16] i.e., $\chi_c < \chi_{ab}$, a very small value of μ_{Pr}, and temperature independence of χ at $T < 20$ K are in strong disagreement with our results. So, our data can be considered as a further evidence for the 3+ valence of Pr in Pr-123 with the scheme of levels proposed in Refs. [2] or [21].

The anisotropy of χ is clearly seen in Figs. 1 and 2A. The degree of magnetic anisotropy $\Delta\chi/\chi_{ab} = (\chi_c - \chi_{ab})/\chi_{ab}$ is $\approx$10% at T=300 K and increases with decreasing temperature to the value $\approx$60% at T=15 K (see the inset of Fig. 2A). This value is considerably larger, than that reported for crystals grown in alumina crucibles [12,13] ($\approx$10% at T=5 K).

In Fig. 2A distinct kinks in $\chi(T)$ are clearly visible for the both field directions. Earlier, the anomaly at T_{N} for oxygen rich Pr-123 could be seen only in the temperature dependence of the derivative [12] $\mathrm{d}\chi(\mathrm{T})/\mathrm{dT}$ and in the anisotropy of $\chi(T)$ [13] but not for the $\chi(T)$ dependence itself. (It should be pointed out, that the corresponding anomaly in $\chi(T)$ at T_{N} was observed for oxygen depleted Pr-123 crystals [13].) The maxima in the $|\mathrm{d}\chi/\mathrm{dT}|$ vs T dependencies marked by the arrow in Fig. 2B are located at $T \approx 15$ K. In accordance with [4,5] we consider the position of the maximum as T_{N}. This value is slightly lower than the usually cited [4] value of T_{N}=17 K. However, depending on sample preparation techniques and methods of measurements, the value of T_{N} varies from 11 to 20 K [4,5,2,13,15,17] even for oxygen rich compounds. For oxygen reduced samples values of $T_{\mathrm{N}} \leq 11$ K were reported [13–15,23]. It is well known, that it is difficult to oxidize the cuprates single crystals. Therefore, oxygen deficiency could be a reason for the lower value of T_{N} for our crystals.

The data obtained for the two directions of H after zero field cooling ZFC have been marked by the open symbols connected by lines in both parts of Fig. 2. Unexpectedly, field cooling FC from T=40 K in a field of H=20 kOe for $H||ab$-plane suppresses fully the anomaly in $\chi_{ab}(T)$ (solid symbols in lower curves in Figs. 2A and B). At the same time FC for $H||c$-axis even in a field of H=48 kOe has no influence on $\chi_c(T)$ and $|\mathrm{d}\chi_{\mathrm{ab}}(\mathrm{T})/\mathrm{dT}|$ curves (solid symbols in upper curves). For $H||ab$-plane the influence of FC in one order of magnitude smaller field, H=5 kOe, on $|\mathrm{d}\chi_{\mathrm{ab}}(\mathrm{T})/\mathrm{dT}|$ curve was observed

(not shown here). After ZFC the field itself does not destroy the kink in $\chi(T)$. Only a decrease of the peak in the $|\mathrm{d}\chi_{\mathrm{c}}(\mathrm{T})/\mathrm{dT}|$ curve was observed by increasing the field. This decrease is more pronounced for $H||ab$-plane. It should be underlined, that FC has not only an effect on $\chi(T)$ curves but, in the case of $H||ab$-plane, it *nearly completely suppresses* the anomaly in the $\chi_{ab}(T)$ dependence suggesting the suppression of AFM ordering of the Pr magnetic moments by FC in $H||ab$-plane.

The distinct anomaly in the $\chi(T)$ dependence for our high quality single crystals makes it possible to see clearly a decrease of T_{N} with increasing field, see Fig. 3. Earlier, a shift $\Delta T_{\mathrm{N}} = T_{\mathrm{N}}(H) - T_{\mathrm{N}}(0)$ was not observed in $\chi(T)$ experiments in fields up to 90 kOe [5,2] contrary to the results of specific heat measurements [2,11] which clearly indicated such a shift. Our results are in good agreement with the specific heat data of Uma *et al.*, [11] obtained on crystals with $T_{\mathrm{N}}(0)$=16.6 K, and with the proposed by them $\Delta T_{\mathrm{N}} \sim H^2$ dependence.

We have also studied the isothermal magnetization of the Pr-123 crystals at 1.7 K $\leq T \leq$ 40 K. Some of the obtained results are shown in Fig. 4A for the both directions of field. At all temperatures the $M(H)$ dependencies are nearly linear and the magnetic anisotropy is more pronounced at lower temperatures. For comparison the magnetization curves of a $\mathrm{Y_{0.4}Pr_{0.6}Ba_2Cu_3O_{7-y}}$ (YPr-123) single crystal [24] grown under the same conditions are also shown for T=5 K. The $M_c(H)$ curve for YPr-123 is close to the corresponding $M_c(H)$ curve for Pr-123, whereas the $M_{ab}(H)$ curve for YPr-123 lies somewhat higher giving a smaller degree of the magnetic anisotropy. The stronger magnetic anisotropy for the pure Pr-123 may be caused by some anisotropic (e.g. pseudodipolar) type of interaction between the $\mathrm{Pr^{3+}}$ ions because the crystal fields acting on $\mathrm{Pr^{3+}}$ should not be affected by the dilution of Pr by Y.

Analyzing the derivative of $M_{ab}(H)$ we observed a change in the behavior at certain transition fields H^* marked in Fig. 4B by vertical arrows. Whereas $\mathrm{dM_{ab}(H)/dH}$ is almost constant at low fields, $H < H^*$, it decreases for $H > H^*$. For the sake of simplicity the low and high field parts of the data were approximated by straight lines as shown on Fig. 4B. Careful analysis of $\mathrm{dM_{ab}(H)/dH}$ curves at T=1.7 K, 2.7 K (not shown in the picture), and 5 K has revealed the tendency of $\mathrm{dM_{ab}(H)/dH}$ to increase with increasing field just below H^*. A more rapid increase of M and hence an increase of $\mathrm{dM(H)/dH}$ below the transition field is a characteristic feature of field induced phase transitions (FIPT) [25]. The observed behavior can be considered as an indication on a weak FIPT in Pr-123 at transition field H^* (probably of spin-reorientation type). The exact nature of this transition has to be settled.

Similarly as the anomaly in the $\chi_{ab}(T)$ dependence this FIPT can be suppressed by FC in $H||ab$-plane. It can be seen from the $\mathrm{dM_{ab}(H)/dH}$ depen-

dence obtained at T=5 K after FC and shown on Fig. 4B by crosses connected by dotted lines. Obviously there is no indication of a FIPT for this curve. The FC $\mathrm{dM_{ab}(H)/dH}$ curve for Pr-123 measured at T=5 K is similar to the corresponding ZFC curve for the YPr-123 crystal (not shown in the picture), for which no anomaly in $\chi(T)$ was observed even after ZFC.

It should be also noted, that the field dependence of the anisotropy parameter $\Delta M/M_{ab} = (M_c(H) - M_{ab}(H))/M_{ab}(H)$ at T=5 K has a clearly visible minimum at $H \approx 30$ kOe (marked by vertical arrow in the inset of Fig. 4A), that is very close to $H^*(5\text{ K})$ obtained from the $\mathrm{dM_{ab}(H)/dH}$ curve shown in Fig. 4B. This minimum can be considered as another manifestation of FIPT in Pr-123. On the other hand, the $\Delta M/M_{ab}$ vs H curve for YPr-123 (see the inset of Fig. 4A) does not indicate any transition.

The FIPT was observed also for $H||c$-axis, the value of $H^*(T)$ being about two times higher, than for $H||ab$-plane. A magnetic phase diagram for the FIPTs in Pr-123 is shown in Fig. 5. The estimation of $H^*(0)$ for $H||ab$-plane gives 31 kOe. The observed FIPTs are very weak. Therefore, a more complicated phase diagram can not be excluded.

For the interpretation of the observed results the mentioned above model [17] of the coupled Cu and Pr sublattices can be used. In that model the Pr ordering is accompanied by the reorientation of the Cu magnetic structure due to the Pr-Cu magnetic interaction. (Very recently it was found [26], that Pr sublattice in fact orders in a long period incommensurate structure just below T_{N} and reorders to commensurate AFM structure at lower temperatures.) Since the influence of FC has been observed by us only for $H||ab$-plane, it should be connected with Cu moments, lying in the ab-plane [15,17]. At the same time, the weak FIPTs observed at $T < T_{\mathrm{N}}$ for both directions of H are connected most probably with the reorientation transitions of Pr moments, tilted away from the c axis [14,15,17]. The mechanism of the proposed suppression of Pr^{3+} AFM ordering by FC in $H||ab$-plane may be as follows. During FC the Cu moments could be frozen by sufficiently strong $H||ab$-plane. Freezing of Cu magnetic moments hinders the AFM ordering in the Pr sublattice due to coupling with the magnetic Cu sublattice. There are some indications on frustration in the Cu magnetic structure as well as on short range ordering in the Cu sublattice [17]. Therefore, it may be favorable for the Cu moments to freeze during FC in $H||ab$-plane. So, the observed behaviour can be considered as an evidence for the existence of considerable coupling between the Cu and Pr magnetic sublattices in Pr-123.

4 Conclusion

We have observed for Pr-123 single crystals a large magnetic anisotropy and a kink in the $\chi(T)$ dependence, connected with Pr AFM ordering. A practically complete suppression of the kink after FC in $H||ab$ was found. At the same time this anomaly remained uninfluenced by FC in $H||c$. A possible explanation of these observations is connected with the magnetic coupling between the Cu and Pr sublattices and the suppression of AFM ordering in the Pr sublattice by freezing of Cu moments, lying in the ab-plane, caused by FC in $H||ab$. Weak FIPTs found for both directions of H are connected most probably with a Pr^{3+} spin-reorientation.

Acknowledgements

We thank S.-L. Drechsler and M. Wolf for discussions. This work was supported by RFBR grants 96-02-00046G, 96-02-16305a; DFG grant MU1015/4-1.

References

[1] H. B. Radousky, J. Mater. Res. 7 (1992) 1917.

[2] G. Hilscher *et al.*, Phys. Rev. B 49 (1994) 535.

[3] M. Merz *et al.*, Phys. Rev. B 55 (1997) 9160.

[4] W-H. Li *et al.*, Phys. Rev. B 40 (1989) R5300.

[5] A. Kebede *et al.*, Phys. Rev. B 40 (1989) 4453.

[6] D. W. Cook *et al.*, Phys. Rev. B 41 (1990) R4801.

[7] Z. Zou, J. Ye, K. Oka, and Y. Nishihara, Phys. Rev. Lett. 80 (1998) 1074.

[8] H. A. Blackstead *et al.*, Phys. Rev. B 54 (1996) 6122.

[9] V. N. Narozhnyi and S.-L. Drechsler, Phys. Rev. Lett. (to be published 14 December 1998).

[10] Y. Zhuo *et al.*, Phys. Rev. B 56 (1997) 8381.

[11] S. Uma *et al.*, J. Appl. Phys. 81 (1997) 4227.

[12] B. Jayaram *et al.*, Phys. Rev. B 52 (1995) 89.

[13] S. Uma *et al.*, Phys. Rev. B 53 (1996) 6829.

[14] J. A. Hodges *et al.*, Physica C 218 (1993) 283.

[15] A. Longmore *et al.*, Phys. Rev. B 53 (1996) 9382.

[16] K. Nehrke and M. W. Pieper, Phys. Rev. Lett. 76 (1996) 1936.

[17] A. T. Boothroyd *et al.*, Phys. Rev. Lett. 78 (1997) 130.

[18] A. T. Boothroyd, Physica B 241-243 (1998) 792.

[19] V. N. Narozhnyi and T. G. Uvarova, J. Magn. Magn. Mater. 157/158 (1996) 675.

[20] A. Erb, E. Walker, and R. Flükiger, Physica C 258 (1996) 9.

[21] A. T. Boothroyd, S. M. Doyle, and R. Osborn, Physica C 217 (1993) 425.

[22] L. Soderholm, C.-K. Loong, G. L. Goodman, and B. D. Dabrowski, Phys. Rev. B 43 (1991) 7923.

[23] A. Kebede *et al.*, J. Appl. Phys. 69 (1991) 5376.

[24] Complete results of investigation of YPr-123 as well as GdPr-123 crystals will be published elsewhere.

[25] A. K. Zvezdin, in *Handbook of magnetic materials*, edited by K. H. J. Buschow, Elsevier, Amsterdam, 1995.

[26] J.P. Hill *et al.*, Phys. Rev. B 58 (1998) 11211.

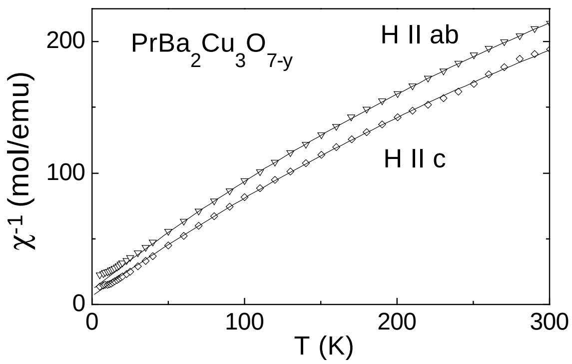

Fig. 1. χ^{-1} vs T for Pr-123 single crystal for $H||ab$-plane and $H||c$-axis. The lines show the modified Curie-Weiss law fitted to the experimental data at 50 K $\leq T \leq$ 300 K.

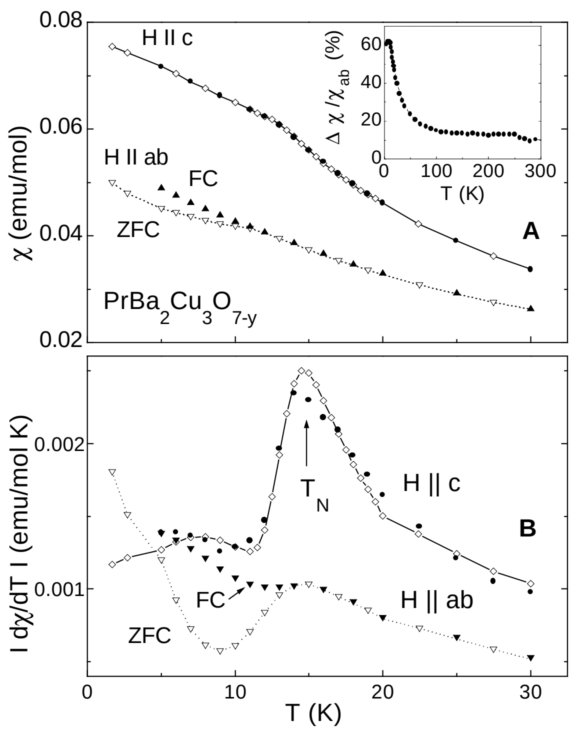

Fig. 2. (A) χ vs T and (B) the absolute value of the susceptibility derivative $|\mathrm{d}\chi(\mathrm{T})/\mathrm{dT}|$ vs T for a Pr-123 single crystal for two directions of H. Solid and dotted lines connecting ZFC data (open symbols) are guides for the eye. Solid symbols in both parts of the figure represent the data measured at H=20 kOe after FC in H=20 kOe ($H \parallel ab$-plane) and in H=48 kOe ($H \parallel c$-axis). The inset shows the anisotropy parameter $(\chi_c - \chi_{ab})/\chi_{ab}$ vs T.

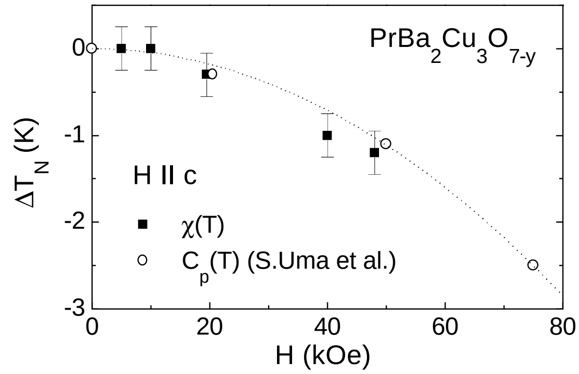

Fig. 3. Decrease of T_{N} of Pr-123 single crystals for $H \parallel c$-axis. Open symbols are the results of specific heat measurements of Uma *et al.* [11]. The dotted line shows the best fit of Uma's data to a $\Delta T_{\mathrm{N}} \sim H^2$ dependence.

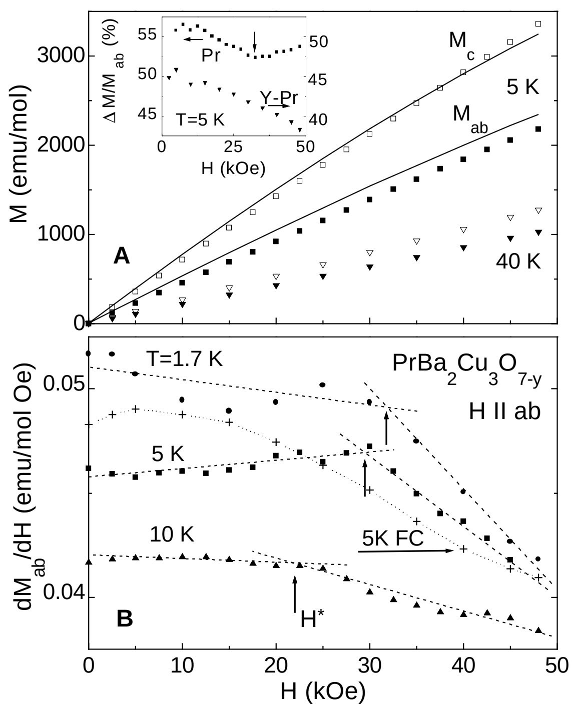

Fig. 4. (A) Isothermal magnetization of a Pr-123 single crystal vs H for the two field directions at T=5 K and 40 K. Solid lines show the magnetization (in emu/mol Pr) of a $\mathrm{Y_{0.4}Pr_{0.6}Ba_2Cu_3O_{7-y}}$ (YPr-123) single crystal. (B) Field derivative of the in-plane magnetization $\mathrm{dM_{ab}(H)/dH}$ vs H for Pr-123 single crystal at T=1.7, 5, and 10 K after ZFC. Lines represent the linear fits to the low and high field parts of the data. Vertical arrows mark the transition fields H^*. Crosses connected by dotted lines show the results obtained at T=5 K after FC in H=20 kOe. The inset shows the normalized anisotropy in magnetization $(M_c - M_{ab})/M_{ab}$ vs H at T=5 K for Pr-123 and YPr-123 single crystals obtained after ZFC.

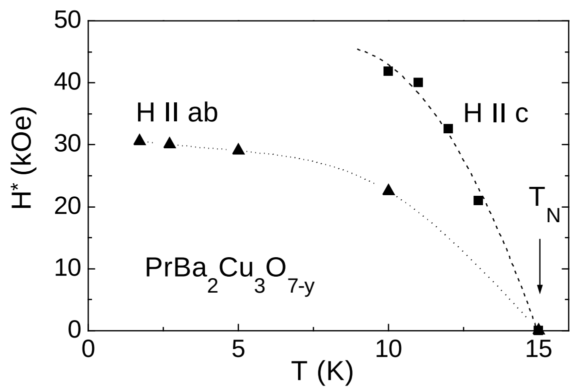

Fig. 5. Transition field H^* (determined as shown by arrows in Fig. 4B) vs T for two directions of H. Lines are guides for eye.